

CLAIMS:

1. A particle comprising:  
a particulate substrate; and  
a thermoplastic elastomer present on or in the substrate in an amount sufficient to improve the dust suppression of the particle above that which would occur if the thermoplastic elastomer was absent.
2. The particle of claim 1, wherein the thermoplastic elastomer has a glass transition temperature of at most about 50 degrees C.
3. The particle of claim 1, wherein the thermoplastic elastomer comprises an amorphous polymer having a glass transition temperature of at most about 50 degrees C.
4. The particle of claim 1, wherein the thermoplastic elastomer comprises a semi-crystalline polymer having a softening point in the range of 40 to 80 degrees C.
5. The particle of claim 1, having an absence of thermosetting resin.
6. The particle of claim 1, wherein the substrate is selected from at least one member of the group consisting of sand, ceramic particles, nut flour, and glass beads.
7. The particle of claim 1, further comprising at least one layer of a thermosetting resin coating substantially surrounding the substrate to form a coated particle.
8. The particle of claim 7, wherein at least one said layer of a thermosetting resin coating further comprises filler particles.

9. The particle of claim 1, wherein the thermoplastic elastomer is selected from the group consisting of homopolymers of C1-C12 alkyl(meth)acrylates, copolymers of olefins such as ethylene or propylene with C1-C12 alkyl(meth)acrylates with other acrylates, or styrene and anhydrides, and butadiene homopolymers and butadiene-acrylonitrile copolymers with or without functionality at their chain ends, and blends and mixtures thereof.

10. The particle of claim 7, wherein the thermosetting resin is a phenol-aldehyde, epoxy, urea-aldehyde, furfuryl alcohol, melamine-aldehyde, polyester, alkyd, novolac, furan resin, or a combination comprising at least one of the foregoing thermosetting resins.

11. The particle of claim 1, wherein the particulate substrate comprises a single particle.

12. The particle of claim 1, wherein the substrate is a composite particle comprising binder and filler particles homogeneously disbursed throughout the binder.

13. The particle of claim 12, wherein the elastomer is located on a surface of the composite particle.

14. The particle of claim 1, wherein the thermoplastic elastomer comprises a member selected from the group consisting of ethylene-n-butyl acrylate copolymer, n-butyl acrylate homopolymer and mixtures thereof.

15. The particle of claim 1, wherein the thermoplastic elastomer comprises a total amount of polyvinyl acetal and polyvinyl formal of not more than 10 weight % of the thermoplastic elastomer on a dry basis.

16. The particle of claim 1, wherein the thermoplastic elastomer comprises a member selected from the group consisting of butadiene homopolymers and butadiene-acrylonitrile copolymers.

17. The particle of claim 1, wherein the thermoplastic elastomer comprises a

member selected from the group consisting of butadiene homopolymers and butadiene-acrylonitrile copolymers with functionality at their chain ends having functional groups selected from the group consisting of carboxy, amine, methacrylate and epoxy.

18. The particle of claim 1, wherein the thermoplastic elastomer comprises an ethylene-n-butyl acrylate copolymer having functional groups selected from the group consisting of carboxy, amine, methacrylate and epoxy.

19. The particle of claim 1, wherein the thermoplastic elastomer comprises a polymer selected from the group consisting of: a carboxyl terminated butadiene-acrylonitrile with an acrylonitrile content of about 10%, a Tg of about minus 50 to minus 77 degrees C, a Brookfield viscosity of about 60,000 MPa, and a carboxyl content of about 25%; a methacrylate vinyl terminated butadiene-acrylonitrile copolymer with an acrylonitrile content of about 18%, a Tg of about minus 50 to minus 49 degrees C, and a Brookfield viscosity of about 50000 MPa; an amine terminated butadiene-acrylonitrile copolymer with an acrylonitrile content of about 18%, a Tg of about minus 50 to minus 59 degrees C, and a Brookfield viscosity of about 100000 MPa; or a combination comprising at least one of the foregoing thermoplastic elastomers.

20. The particle of claim 1, wherein the particle has a turbidity of 5 to 200 NTU.

21. The particle of claim 1, wherein the particle contains 0.005 to 4.0 weight percent of the thermoplastic elastomer based upon weight of the particle.

22. The particle of claim 7, wherein the coating contains 0.05 to 100 weight percent of the thermoplastic elastomer based upon weight of the coating.

23. The particle of claim 1, wherein upon being subjected to a 60 minute ball mill test the particle achieves a turbidity measurement of less than 200 NTU at 30 minutes ball mill time and/or less than 300 NTU at 60 minutes ball mill time.

24. The particle of claim 1, wherein upon being subjected to a 60 minute ball mill

test achieves a turbidity measurement of less than 100 NTU at 30 minutes ball mill time and/or less than 150 NTU at 60 minutes ball mill time.

25. The particle of claim 1, further having at least one curable thermosetting resin coating and a UCS of at least 85 % of a control particle which has the same composition but lacks the thermoplastic elastomer.

26. The particle of claim 1, further having at least one precured thermosetting resin coating which reduces the fracture tendency of the coated particle, as measured by a crush resistance test, by at least 20% compared to a control particle which has the same composition except for lacking the thermoplastic elastomer.

27. The particle of claim 1, further having at least one precured thermosetting resin coating which reduces the fracture tendency of the coated particle, as measured by a crush resistance test, by at least 10% compared to a control particle which has the same composition except for lacking the thermoplastic elastomer.

28. The particle of claim 1, having at least one precured thermosetting resin coating and having sufficient thermoplastic elastomer to have a crush strength of at least equal to that of a control particle which has the same composition but lacks the thermoplastic elastomer.

29. The particle of claim 1, wherein the particle displays reduced abrasion towards other particles, handling equipment and/or down hole tubular objects and/or equipment as compared with substrate particles that lack the elastomer.

30. The particle of claim 1, having sufficient thermoplastic elastomer to reduce water pickup by the particle by 20% as compared with a substrate particle that lacks the elastomer.

31. The particle of claim 1, having sufficient thermoplastic elastomer to result in a particle having at least 10 % of a reduction in weight loss under an API RP 56 acid resistance

test as compared to a particle which lacks the elastomer.

32. The particle of claim 1, having sufficient thermoplastic elastomer to be free flowing after 24 hours when stored at 95% relative humidity and 104 degrees F.

33. The particle of claim 1, having sufficient thermoplastic elastomer to be a processing aid which results in reduced agglomeration wherein an amount of clusters and other oversized clumps is reduced so as to have a yield improvement of at least 2-5% of desired in-size particles by reducing agglomerates, as compared to a particle which is the same but lacks the elastomer.

34. The particle of claim 1, wherein the thermoplastic elastomer present on or in the substrate improves the crush resistance and/or the abrasive properties and/or the acid resistance of the particle above that which would occur if the thermoplastic elastomer was absent.

35. A method for manufacturing a particle comprising:  
heating a particulate substrate; and  
disposing upon the particulate substrate, a thermoplastic elastomer in an amount sufficient to improve the dust suppression and / or crush resistance and/or acid resistance and/or abrasion resistance of the particle above that which would occur if the thermoplastic elastomer was absent.

36. The method of claim 35, comprising mixing the thermoplastic elastomer with the substrate after the substrate is heated to temperatures of about 225° to 550°F.

37. The method of claim 35, further comprising the steps of mixing a resin with the particulate substrate preheated to temperatures of about 225° to 550°F, to form a resin coating on the substrate, and then adding the thermoplastic elastomer.

38. The method of claim 35, comprising the steps of mixing the thermoplastic elastomer with the particulate substrate preheated to temperatures of about 225° to 550°F, and then adding additional resin to form a resin coating on the particle.

39. The method of claim 37, wherein the resin is in the form of novolac flakes, and wherein the novolac flakes are added to the preheated substrate to form a mixture and the thermoplastic elastomer is added to the mixture about 30 to 90 seconds after the flakes are added to the substrate.

40. The method of claim 39, wherein the novolac flakes contains filler particulates or the filler particles are added concurrently with the flake.

41. The method of claim 37, wherein the resin is selected from the group consisting of a phenolic resole resin, a furan resin, a terpolymer of phenol, furfuryl alcohol and formaldehyde, and phenol formaldehyde novolac resin and mixtures thereof.

42. The method of Claim 35, wherein the particulate substrate is selected from the group consisting of sand, bauxite, zircon, ceramic particles, nut flour, glass beads, composite particles comprising a resin binder and filler particles, and mixtures thereof and has from about 8 to about 100 mesh in size.

43. A method for producing a particle according to Claim 35, wherein the substrate is a single particle and a coating resin is further applied to the particulate substrate to coat the substrate, the coating resin is cured and the thermoplastic elastomer is then applied to the particle.

44. The method according to Claim 43, wherein after the resin has cured, the particles are coated with additional coating resin and cured again and the thermoplastic elastomer is disposed upon the coating resin.

45. The method according to Claim 44, wherein the resin comprises a resole resin and the coating resin comprises a polyurethane resin or an alkaline modified resole curable with ester.

46. The method according to Claim 35, further comprising granulating the particles.

47. The method of Claim 35, further comprising a resin with filler particles, wherein the filler particles have an average grain size of 4 to 10  $\mu\text{m}$ .

48. A method of treating a hydraulically induced fracture in a subterranean formation surrounding a wellbore comprising introducing a proppant comprising free flowing particles of Claim 1 into the fracture.

49. The method according to Claim 48, wherein a pack comprising the particles is formed in the formation.

50. A method of treating a hydraulically induced fracture in a subterranean formation surrounding a wellbore comprising introducing a proppant comprising free flowing particles of Claim 7 into the fracture.

51. The method according to Claim 50, wherein a pack comprising the particles is formed in the formation.

52. A method for treating a subterranean formation comprising:  
applying to the subterranean formation a hydraulic fracturing fluid and a particulate comprising substrate particulate upon which is disposed a thermoplastic elastomer.

53. The method for treating a subterranean formation of claim 52, wherein the particulate substrate further has a curable coating and wherein the curable coating undergoes curing within fractures of the subterranean formation.

54. The method for treating a subterranean formation of claim 52, further comprising introducing the particles into the well bore forming a gravel pack about a wellbore and about a containment area.

55. A method for treating a subterranean formation comprising:  
applying to the subterranean formation a hydraulic fracturing fluid and a particulate comprising a substrate particulate upon which is disposed a thermoplastic elastomer and a thermosetting resin.

56. The method for treating a subterranean formation of claim 55, further comprising introducing the particles into the well bore forming a gravel pack about a wellbore and about a containment area.

57. A particle comprising:  
a particulate substrate; and  
a thermoplastic elastomer, wherein the particle has a compressive strength retention of greater than about 50% as measured by a UCS test when compared with a particle having the same composition except for the thermoplastic elastomer and a turbidity of about 10 to 200 NTU after a one hour ball mill test.



58. The particle of claim 57, wherein the particle further has a first resin coating and optionally a second resin coating, and wherein the first resin and the second resin are phenol-aldehydes, epoxies, urea-aldehydes, furfuryl alcohols, melamine-aldehydes, polyesters, alkyds, novolacs, furan resins, or a combination comprising at least one of the foregoing resins and wherein an outermost coating of the particle is the thermoplastic elastomer.

59. The particle of claim 58, wherein the first resin coating comprises a first curative in an amount sufficient to at most partially cure the first resin and the second resin coating comprises a second curative in an amount sufficient to at most partially cure the second curable resin coating.

60. A particle comprising:  
a particulate substrate;  
a thermoplastic elastomer; and  
a thermosetting resin, wherein the particle has a compressive strength retention of greater than about 50% as measured by a UCS test when compared with a particle having the same composition except for the thermoplastic elastomer and a turbidity of about 10 to 200 NTU after a one hour ball mill test.

61. A particle comprising:  
a particulate substrate;  
a thermoplastic elastomer; and  
a thermosetting resin, wherein the thermoplastic elastomer is present in an amount sufficient to improve the dust suppression and / or crush resistance and/or acid resistance and/or abrasion resistance of the particle above that which would occur if the thermoplastic elastomer was absent.

62. The particle of claim 61, wherein the thermoplastic elastomer has a glass transition temperature of at most about 50 degrees C.

63. The particle of claim 61, wherein the substrate is selected from at least one

member of the group consisting of sand, ceramic particles, nut flour, and glass beads.

64. The particle of claim 61, further comprising at least one layer of a thermosetting resin coating substantially surrounding the substrate to form a coated particle.

65. The particle of claim 64, wherein at least one said layer of a thermosetting resin coating further comprises filler particles.

66. The particle of claim 61, wherein the thermoplastic elastomer is selected from the group consisting of homopolymers of C1-C12 alkyl(meth)acrylates, copolymers of olefins such as ethylene or propylene with C1-C12 alkyl(meth)acrylates with other acrylates, or styrene and anhydrides, and butadiene homopolymers and butadiene-acrylonitrile copolymers with or without functionality at their chain ends, and blends and mixtures thereof.

67. The particle of claim 61, wherein the thermosetting resin is a phenol-aldehyde, epoxy, urea-aldehyde, furfuryl alcohol, melamine-aldehyde, polyester, alkyd, novolac, furan resin, or a combination comprising at least one of the foregoing thermosetting resins.

68. The particle of claim 61, wherein the substrate particle is a composite particle comprising binder and filler particles homogeneously disbursed throughout the binder.

69. The particle of claim 61, wherein the thermoplastic elastomer is located on a surface of the composite particle.

70. The particle of claim 61, wherein the thermoplastic elastomer forms a blend with the thermosetting resin.

71. The particle of claim 61, wherein the thermoplastic elastomer comprises a member selected from the group consisting of ethylene-n-butyl acrylate copolymer, n-butyl acrylate homopolymer and mixtures thereof.

72. The particle of claim 61, wherein the thermoplastic elastomer comprises a

member selected from the group consisting of butadiene homopolymers and butadiene-acrylonitrile copolymers.

73. The particle of claim 61, wherein the thermoplastic elastomer comprises a member selected from the group consisting of butadiene homopolymers and butadiene-acrylonitrile copolymers with functionality at their chain ends having functional groups selected from the group consisting of carboxy, amine, methacrylate and epoxy.

74. The particle of claim 61, wherein the thermoplastic elastomer comprises an ethylene-n-butyl acrylate copolymer having functional groups selected from the group consisting of carboxy, amine, methacrylate and epoxy.

75. The particle of claim 61, wherein the thermoplastic elastomer comprises a polymer selected from the group consisting of: a carboxyl terminated butadiene-acrylonitrile with an acrylonitrile content of about 10%, a Tg of about minus 50 to minus 77 degrees C, a Brookfield viscosity of about 60,000 MPa, and a carboxyl content of about 25%; a methacrylate vinyl terminated butadiene-acrylonitrile copolymer with an acrylonitrile content of about 18%, a Tg of about minus 50 to minus 49 degrees C, and a Brookfield viscosity of about 50000 MPa; an amine terminated butadiene-acrylonitrile copolymer with an acrylonitrile content of about 18%, a Tg of about minus 50 to minus 59 degrees C, and a Brookfield viscosity of about 100000 MPa; or a combination comprising at least one of the foregoing thermoplastic elastomers.

76. The particle of claim 61, wherein the particle has a turbidity of 5 to 200 NTU.

77. The particle of claim 61, wherein the particle contains 0.005 to 4.0 weight percent of the thermoplastic elastomer based upon weight of the particle.

78. The particle of claim 61, wherein upon being subjected to a 60 minute ball mill test the particle achieves a turbidity measurement of less than 200 NTU at 30 minutes ball mill time and/or less than 300 NTU at 60 minutes ball mill time.

79. The particle of claim 61, wherein the particles, upon being subjected to a 60 minute ball mill test achieves a turbidity measurement of less than 100 NTU at 30 minutes ball mill time and/or less than 150 NTU at 60 minutes ball mill time.

80. The particle of claim 61, further having at least one precured thermosetting resin coating which reduces the fracture tendency of the coated particle, as measured by a crush resistance test, by at least 20% compared to a control particle which has the same composition except for lacking the thermoplastic elastomer.

81. The particle of claim 61, having at least one precured thermosetting resin coating and having sufficient thermoplastic elastomer to have a crush strength of at least equal to that of a control particle which has the same composition but lacks the thermoplastic elastomer.

82. The particle of claim 61, wherein the particle displays reduced abrasion towards other particles, handling equipment and/or down hole tubular objects and/or equipment as compared with substrate particles that lack the elastomer.

83. The particle of claim 61, having sufficient thermoplastic elastomer to reduce water pickup by the particle by 20% as compared with a substrate particle that lacks the elastomer.

84. The particle of claim 61, having sufficient thermoplastic elastomer to result in a particle having at least 10 % of a reduction in weight loss under an API RP 56 acid resistance test as compared to a particle which is the same but lacks the elastomer.

85. The particle of claim 61, having sufficient thermoplastic elastomer to result in particles that are flowable after 24 hours of being stored at 95% relative humidity and 104 degrees F.

86. The particle of claim 61, having sufficient thermoplastic elastomer to be a processing aid resulting in reduced agglomeration wherein an amount of clusters and other oversized clumps is reduced to have a yield improvement of at least 2-5% of desired in-size particles by reducing agglomerates, as compared to a particle which is the same but lacks the elastomer.

87. A method for manufacturing a particle comprising:  
heating a particulate substrate;  
disposing upon the particulate substrate, a thermosetting resin; and  
disposing upon the particulate substrate and/or the thermosetting resin, a thermoplastic elastomer in an amount sufficient to improve the dust suppression and / or crush resistance and/or acid resistance and/or abrasion resistance of the particle above that which would occur if the thermoplastic elastomer was absent.

88. A particle comprising:  
a substantially homogeneous formed particle comprising:  
a core comprising a binder and filler particles dispersed throughout the binder, wherein particle size of the filler particles ranges from about 0.5 to about 60  $\mu\text{m}$ ; wherein the particle has a bulk density of 0.50 to 1.30 grams per cubic centimeter, and a grain density of 0.90 to about 2.2  $\text{gr}/\text{cm}^3$ ; optionally the particle has a resin coating; and  
a thermoplastic elastomer, wherein the thermoplastic elastomer has a glass transition temperature of at most 50 degrees C and is selected from the group consisting of homopolymers of C1-C12 alkyl(meth)acrylates, copolymers of olefins selected from the group consisting of ethylene and propylene with C1-C12 alkyl(meth)acrylates, butadiene homopolymers and butadiene-acrylonitrile copolymers, and a semicrystalline polymer.

89. A proppant pack comprising the particles of claim 1, after the particles are placed in a well bore.

90. A proppant pack comprising the particles of claim 7, after the particles are placed in a well bore.

91. A proppant pack comprising the particles of claim 57, after the particles are placed in a well bore.

92. A proppant pack comprising the particles of claim 60, after the particles are placed in a well bore.

93. A proppant pack comprising the particles of claim 61, after the particles are placed in a well bore.

94. A proppant pack comprising the particles of claim 88, after the particles are placed in a well bore.

95. A foundry particle comprising the particles of Claim 1.

96. A foundry core or mold comprising the particles of Claim 1.

97. A foundry particle comprising the particles of Claim 7.

98. A foundry core or mold comprising the particles of Claim 7.

99. A foundry particle comprising the particles of Claim 61.

100. A foundry core or mold comprising the particles of Claim 61.